Acids and Bases

- acid – H appears in the formula
- base – contains OH^- group

- acid + base $\rightarrow$ salt + H_2O
- $HCl + NaOH \rightarrow NaCl + H_2O$

Acids

- In aqueous solution have the following properties:
  - sour taste
  - turn blue litmus paper red
  - neutralise bases

Bases

- In aqueous solution have the following properties:
  - bitter taste
  - soapy feeling
  - turn red litmus paper blue
  - neutralise acids

Arrhenius Acids and Bases

- An Arrhenius acid is a substance that, when dissolved in water, increases the concentration of hydronium ions, $H_3O^+(aq)$.
- An Arrhenius base is a substance that, when dissolved in water, increases the concentration of hydroxide ions, $OH^-(aq)$.

Hydronium ion

- The hydrogen ion is a bare proton, but in water solution it is hydrated and exists as the hydronium ion (H_3O^+).
- $$\mathrm{H^+ + \; :\underset{\substack{\cdot\cdot\\ H}}{\ddot{O}}:H \;\rightarrow\; H:\underset{\substack{\cdot\cdot\\ H}}{\ddot{O}}:H^+}$$
- When we write $H^+(aq)$ or just H^+ we understand it is hydrated.

Common acids

- HCl
- H_2SO_4
- HNO_3
- CH_3COOH
- Polar covalent molecules in the pure anhydrous state
- When dissolved in water form ions:

  $HCl(g) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$

Nonmetal Oxides as Acids

- nonmetal oxide + H_2O $\rightarrow$ oxyacid

  $SO_3 + H_2O \rightarrow H_2SO_4$

Bases

- Ionic compounds that contain OH^- or O^{2-}
- $NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$
- metal oxide + $H_2O \rightarrow$ metal hydroxide

  $CaO + H_2O \rightarrow Ca(OH)_2$
- molecular bases

  $NH_3(aq) + H_2O \rightarrow NH_4^+(aq) + OH^-(aq)$

Strong and weak acids and bases

- Strong acid or base is one that is completely ionised in water (strong electrolyte).
- Strong acids – HCl, H_2SO_4, HNO_3, HBr, HI, $HClO_4$, $HBrO_4$
- weak acids - CH_3COOH
- Weak acid or base is one that is only partially ionised in water (weak electrolyte).
- Strong bases – contain OH^- (strong electrolyte)
- Weak base – typically contains nitrogen

Example

- Identify each of the following as an Arrhenius acid or base. Give the chemical equation for the reaction of the substance with water, showing the origin of the acidity or basicity.

(a) BaO

(b) H_2S

Solution

- $BaO + H_2O \rightarrow Ba^{2+} + 2OH^-$
- base

- $H_2S + H_2O \rightarrow H_3O^+ + HS^-$
- acid

Brønsted-Lowry Acids and Bases

- More general definition
- Not limited to aqueous solutions

- B.L. acid – proton donor
- B.L. base – proton acceptor

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

acid base acid base

conjugate pair

conjugate pair

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

base acid acid base

conjugate pair

conjugate pair

Conjugate acid-base pairs differ from each other by only **one** proton.

Conjugate pairs

- For conjugate acid-base pairs, the stronger the acid, the weaker is its conjugate base, and vice versa.
- HCl is a strong acid but Cl^- is a weak base

Example

- Formic acid, $HCHO_2$, is a stronger acid than acetic acid, CH_3COOH. Which of the following is the stronger base, CHO_2^- or CH_3COO^-?

Acid and Base Strength

- In any acid-base reaction, the equilibrium will favour the reaction that moves the proton to the stronger base.
- $HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$
- H_2O is a much stronger base than Cl^-, so the equilibrium lies so far to the right that K cannot be measured (K>>1).

Amphoteric Substances

- Some substances can act as acids or bases (amphoteric).
- Water behaves as a base (proton acceptor) toward HCl and as an acid toward NH_3 (proton donor).
- HSO_4^- and HCO_3^- are amphoteric
- In Arrhenius definition HCO_3^- can only act as an acid.

Example

- Classify the following as an Arrenhius acid or base, Brønsted-Lowry acid or base:
  - $HClO_4$
  - HSO_4^-
- Classify each of the following as a weak acid or base, or strong acid or base:
  - HNO_3
  - HCO_3^-
  - NH_3

Example

- For the following reactions, label all the species as Brønsted-Lowry acids or bases. Indicate the species that are conjugates of one another:

(a) $HPO_4^{2-} + NH_4^+ \rightleftharpoons NH_3 + H_2PO_4^-$

(b) $SO_4^{2-} + H_2O \rightleftharpoons HSO_4^- + OH^-$

Ionization of Water

- Even the most highly purified water possesses a small but definite conductivity. Water must therefore be slightly ionised,

$$H_2O \rightleftharpoons H^+ + OH^-$$

- Strictly speaking the hydrogen ion H^+ exists in water as the hydronium ion, H_3O^+. The dissociation of water should therefore really be written as

$$2H_2O \rightleftharpoons H_3O^+ + OH^-.$$

- Then,

$$K_c = \frac{[H^+][OH^-]}{[H_2O]^2}$$

- Since the water is only slightly ionized, the molar concentration of water has essentially a constant value of 55.6 mol dm^{-3}. Therefore the term $[H_2O]^2$ is a constant which we combine with K_c.

$$[H^+][OH^-] = K_c \times [H_2O]^2$$

$$[H^+][OH^-] = \text{constant} = K_w$$

- $K_w \equiv$ ionic product of water

- K_w varies with temperature.
- At 25 °C, $K_w = 1.008 \times 10^{-14}$ but is usually taken as 1.00×10^{-14}.
- If the product of $[H^+]$ and $[OH^-]$ in aqueous solution momentarily exceeds this value, the excess ions immediately combine to form water. Similarly, if the product of the two ionic concentrations is momentarily less than 10^{-14} more water molecules will dissociate until the equilibrium value is attained.

- In pure water, $[H^+] = [OH^-] = \sqrt{K_w}$
$= 10^{-7}$ mol dm^{-3}

- A solution in which $[H^+] = [OH^-]$ is a neutral solution.

- If $[H^+] > 10^{-7}$ mol dm^{-3} the solution is acidic, and if $[H^+] < 10^{-7}$ mol dm^{-3} the solution is alkaline (or basic).

- If $[OH^-] > 10^{-7}$ mol dm^{-3} the solution is alkaline; if $[OH^-] < 10^{-7}$ mol dm^{-3} the solution is acidic.

$$[H^+] = \frac{K_w}{[OH^-]} \quad \text{or} \quad [OH^-] = \frac{K_w}{[H^+]}$$

- Hence measurement of either $[H^+]$ or $[OH^-]$ yields the other.

pH, pOH and pK_w

$$pH = -\log_{10}[H^+]$$
$$pOH = -\log_{10}[OH^-]$$

$$K_w = [H^+][OH^-]$$
$$\log K_w = \log[H^+] + \log[OH^-]$$
$$-\log K_w = -\log[H^+] + (-\log[OH^-])$$
$$\boxed{pK_w = pH + pOH}$$

At 25 °C $pK_w = pH + pOH = 14$

- neutral solution: $pH = pOH = 7$
- acidic solution: $pH < 7$ $pOH > 7$
- alkaline solution: $pH > 7$ $pOH < 7$

Example

- Find the pH of a solution for which $[H^+]$ = 4.00×10^{-5} mol dm^{-3}.

$$
\begin{aligned}
pH &= -\log[H^+] \\
&= -\log(4.00 \times 10^{-5}) \\
&= -(-4.398) \\
&= 4.398
\end{aligned}
$$

Example

- Find the hydrogen ion concentration corresponding to pH = 5.643.

$$
\begin{aligned}
pH = -\log[H^+] &= 5.643 \\
\log[H^+] &= -5.643 \\
[H^+] &= 10^{-5.643} \\
&= 2.28 \times 10^{-6} \text{ mol dm}^{-3}
\end{aligned}
$$

Acid Dissociation Constant, K_a

- For a weak acid HA:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

or

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

- acid dissociation constant, K_a

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

- The larger the value of K_a, the stronger is the acid (more ions).

$$\boxed{pK_a = -\log K_a}$$

Base Ionization Constant, K_b

- For a weak base B:
  $B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$

- base ionisation constant, K_b

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

- $pK_b = -\log K_b$
- The larger is the value of K_b, the stronger is the base.

Neutralisation of a strong acid and a strong base

- Start with 100 cm^3 of 1.00 mol dm^{-3} HCl and add 1.00 mol dm^{-3} NaOH.

$$HCl + NaOH \rightarrow NaCl + H_2O$$

- Equivalence point – occurs when 100 cm^3 of base have been added.

pH at start

Since HCl $\rightarrow$ $H^+ + Cl^-$,

$[H^+] = [HCl]$

$\therefore$ pH = -log[H^+]

= -log[1.00]

= **0**

pH before equivalence point

Determined by amount of acid not yet reacted with base.

When 50.0 cm^3 of NaOH have been added,

total moles HCl = 1.00 mol dm^{-3} x 0.100 dm^3 = 0.100 mol
moles OH^- added = 1.00 mol dm^{-3} x 0.0500 dm^3
= 0.0500 mol
moles H^+ unreacted = 0.100 – 0.0500 mol = 0.0500 mol
total volume = 100 + 50.0 cm^3 = 150 cm^3 = 0.150 dm^3

$$[H^+] = \frac{0.0500\ \text{mol}}{0.150\ \text{dm}^3} = 0.333\ \text{mol dm}^{-3}$$

pH = -log[H^+] = -log(0.333) = **0.477**

pH at equivalence point

- Have a solution of NaCl in water and as neither Na^+ nor Cl^- react with H_2O
- pH = **7.00**.

pH after equivalence point

Determined by amount of excess base added.

When 150 cm^3 of NaOH have been added,

excess volume NaOH added = 150 – 100 cm^3

= 50 cm^3

$$\text{excess}\,[OH^-] = \frac{1.00 \times 0.0500\ \text{mol}}{0.250\ \text{dm}^3} = 0.200\ \text{mol dm}^{-3}$$

pOH = –log[OH^-] = –log(0.200) = 0.699

pH = 14 – pOH = 14 – 0.699 = **13.301**

pH Calculations for Weak Acids

e.g. HCOOH $K_a = 2.1 \times 10^{-4}$
formic acid
CH_3COOH $K_a = 1.8 \times 10^{-5}$
acetic acid

- Formic acid is a stronger acid than acetic acid because K_a indicates that it ionizes more (K_a larger).

Calculating K_a from the pH

- The pH of a 0.10 mol dm^{-3} solution of formic acid, HCOOH, at 25 °C is 2.38. Calculate K_a for formic acid at this temperature.

Solution

$HCOOH \rightleftharpoons H^+ + HCOO^-$

pH = $-\log[H^+]$ = 2.38

$\log[H^+] = -2.38$

$[H^+] = 10^{-2.38}$

$= 4.2 \times 10^{-3}$ mol dm^{-3}

$= [HCOO^-]$

	$HCOOH$	$\rightleftharpoons$ H^+	+ $HCOO^-$
Initial	0.10	0	0
Change	-4.2×10^{-3}	$+4.2 \times 10^{-3}$	$+4.2 \times 10^{-3}$
Equi.	$0.10-4.2 \times 10^{-3}$	$+4.2 \times 10^{-3}$	$+4.2 \times 10^{-3}$

$$K_a = \frac{[H^+][HCOO^-]}{[HCOOH]}$$

$$= \frac{(4.2\times10^{-3})(4.2\times10^{-3})}{(0.10-4.2\times10^{-3})}$$

$$= 1.8\times10^{-4}$$

Percent Ionisation

$$\text{percent ionisation} = \frac{[\mathrm{H^+}]_{\text{eq}}}{[\mathrm{HA}]_{\text{initial}}} \times 100$$

$$= \frac{4.2 \times 10^{-3}}{0.10} \times 100$$

$$= 4.2\%$$

Example

- Calculate the pH of a 0.050 mol dm^{-3} nitrous acid (HNO_2) solution.

Solution

Let x = conc. of HNO_2 that ionizes.

	HNO_2	$\rightleftharpoons$	H^+	+	NO_2^-
Initial Conc.	0.050		0		0
Equi≡ Conc.	$0.050 - x$		x		x

$$K_a = \frac{[H^+][NO_2^-]}{[HNO_2]} = 4.5 \times 10^{-4}$$

$$\frac{x^2}{0.050 - x} = 4.5 \times 10^{-4}$$

Assume x is small compared to 0.050, then

$$\frac{x^2}{0.050} \approx 4.5 \times 10^{-4}$$

$$x = 4.8 \times 10^{-3} \text{ mol dm}^{-3}$$

Test approximation:

$$\frac{0.0048}{0.050} \times 100\% = 9.6\%$$

i.e. more than 5% of original concentration so must solve quadratic equation.

$$x^2 + 4.5 \times 10^{-4}\, x - 2.3 \times 10^{-5} = 0$$

$$x = 4.6 \times 10^{-3} \text{ mol dm}^{-3}$$

$$= [H^+]$$

$$\text{pH} = -\log (4.6 \times 10^{-3})$$

$$= \mathbf{2.34}$$

pH Calculations for Weak Bases

NH_3 $K_b = 1.8 \times 10^{-5}$

Example

What is the pH of a 0.10 mol dm^{-3} solution of NH_3? What is α, the degree of ionisation, for this solution?

Solution

Let x = conc. of NH_3 that ionizes.

	$NH_3 + H_2O$	$\rightleftharpoons$ NH_4^+	$+ OH^-$
Initial Conc.	0.10	0	0
Equi≡. Conc.	$0.10 - x$	x	x

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

$$\frac{x^2}{0.10 - x} = 1.8 \times 10^{-5}$$

Assume x is small compared to 0.10, then

$$\frac{x^2}{0.10} \approx 1.8 \times 10^{-5}$$

$$x = 1.34 \times 10^{-3} \text{ mol dm}^{-3}$$

Test approximation:

$$\frac{1.34 \times 10^{-3}}{0.10} \times 100\% = 1.34\% < 5\%$$

∴ approximation valid.

$$[OH^-] = x = 1.34 \times 10^{-3} \text{ mol dm}^{-3}$$

$$pOH = 2.8$$

$$pH = 14 - 2.87$$

$$= \mathbf{11.13}$$

Degree of ionisation, α

$$\alpha = \frac{1.34 \text{ x } 10^{-3}}{0.10} = 1.34 \times 10^{-2}$$

Conjugate acid-base pairs

- The product of the ionization constant for an acid and the ionization constant of its conjugate base is the ionic product of water.

$$\boxed{K_a \text{ x } K_b = K_w}$$

E.g. for hydrofluoric acid

$$HF + H_2O \rightleftharpoons H_3O^+ + F^-$$

$$K_a = \frac{[H_3O^+][F^-]}{[HF]}$$

and for fluoride ion, its conjugate base

$$F^- + H_2O \rightleftharpoons HF + OH^-$$

$$K_b = \frac{[HF][OH^-]}{[F^-]}$$

$$K_a \times K_b = \frac{[H_3O^+][F^-]}{[HF]} \times \frac{[HF][OH^-]}{[F^-]}$$

$$= [H_3O^+][OH^-] = K_w$$